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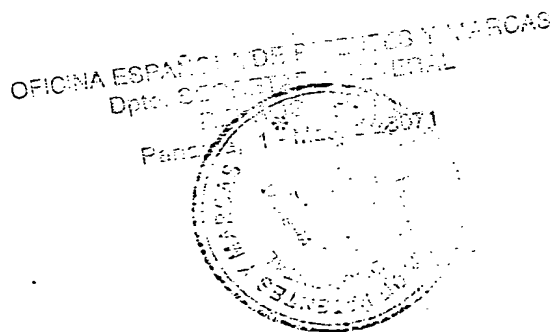
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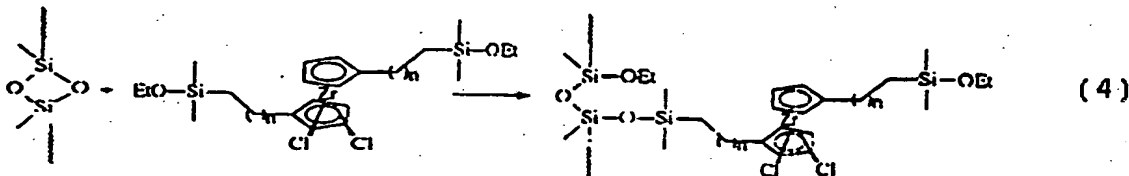
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(54) Title: METHOD FOR PRODUCING SUPPORTED METALLOCENE CATALYST AND OLEFIN POLYMERIZATION PROCESS USING THE SAME



(57) Abstract

Disclosed is a method of manufacturing supported metallocene catalyst as in the reaction formula (4) by reacting of metallocene catalyst having an alkoxysilane group with highly reactive siloxane groups on supporting materials, which is produced when the supporting materials are dried at high temperature, not with surface OH groups. By using this method, various side reactions occurred by the reaction of the metallocene compounds with hydroxyl groups could be eliminated.

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METHOD FOR PRODUCING SUPPORTED METALLOCENE CATALYST AND OLEFIN POLYMERIZATION PROCESS USING THE SAME

CROSS REFERENCE TO RELATED APPLICATION

5 This application is based on application No 98-12660 filed in the Korean Industrial Property Office on April 9, 1998, the content of which is incorporated hereinto by reference.

BACKGROUND OF THE INVENTION

(a) Field of the Invention

10 The present invention relates to method for producing supported metallocene catalyst and olefin polymerization process using the same, and more particularly to a method for manufacturing supported metallocene catalyst by reacting metallocene catalyst having an alkoxysilan group at a part of a ligand with a support having a highly reactive siloxane group at the surface, and the
15 olefin polymerization process using the same.

(b) Description of the Related Art

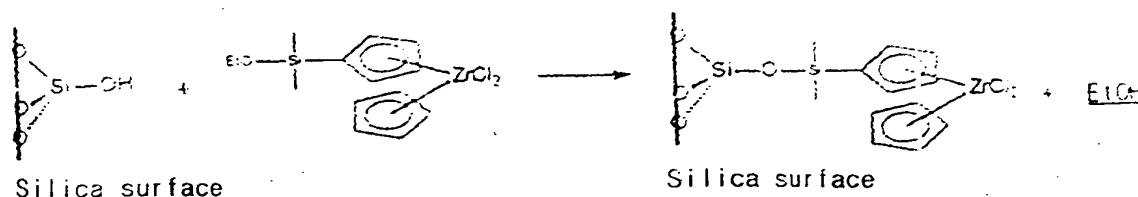
In 1976, Professor Kaminsky of Germany reported that olefin polymerization could be made by using MAO (methylaluminoxane) compound obtained through partial hydrolysis of trimethylaluminum as a cocatalyst and by
20 zirconocendichloride compound as a catalyst (A. Anderson, J. G. Corde, J. Herwing, W. Kaminsky, A. Merk, R. Mottweiler, J. Pein, H. Sinn, and Vollmer, Angew. Chem, Int, Ed. Engl., 15, 630, 1976). This homogeneous catalyst shows unique polymerization characteristics that conventional Ziegler-Natta catalysts can not embody. That is, molecular weight distribution of the
25 produced polymer is narrow, copolymerization is easy, and the second monomer distribution is uniform. Not only molecular weight or the degree of copolymerization can be changed freely by simply changing the catalyst ligand structure, but also tacticity of polymer can be controlled according to the

molecular symmetry of catalyst. These unique characteristics not only opened up a way of new polymers not obtainable through conventional Ziegler-Natta catalyst, but also the way of tailor-made polymers. Accordingly, studies on this catalyst have been actively going on.

5 Polyethylene manufacturing processes are can be classified into the high pressure process, the solution process, the slurry process, and the gas phase process. Efforts to replace only the catalysts of these processes with metallocene catalysts are being made. In the gas phase or slurry processes, particle morphology and bulk density of the produced polymer should be
10 controlled to increase output per reactor unit capacity, and a reactor fouling should be solved for the continuous operation. In order to increase the bulk density and to solve the reactor fouling, supported catalyst should be used in those process. As a result of this, various efforts to support metallocene catalyst on suitable solid material have been made.

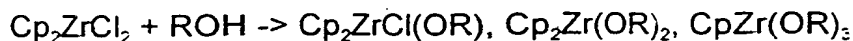
15 One of the supporting methods of the metallocene catalyst is to synthesize metallocene compounds having functional groups such as alkoxysilane group on a part of a ligand and then to react these functional groups with hydroxyl group of the silica (R. Jackson, J. Ruddlesden., and D. J. Thompson, J. Organomet. Chem. 125 (1997), 57; B. L. Booth, G. C. Offumme, C.
20 Stacey, and P. J. T. Tait, J. Organomet. Chem. 315 (1986), 145; European Patent No. 293815). In this case, using silica OH group according to such a reaction is plainly stated in the below reaction formula 1. European Patent No. 293815, page 5, lines 11 to 15 describe that support having an amount of hydroxyl group on its surface of 0.5 ~ 50 mmol/g, particularly 1 ~ 20 mmol/g, and
25 more desirably 1.5 ~ 10 mmol/g, is used.

<Reaction formula 1>



However, when the compounds are reacted with the hydroxy group of the surfaces, the following various side reactions can be accompanied (D. J. Cardin, M. F. Lappert, and C. L. Raston, Chemistry of Organo-Zirconium and Hafnium Compounds, John Wiley & Sons 1986, 96 page).

<Reaction formula 2>



There is a sufficient possibility that this kind of reaction could also occur when the metallocene compounds are reacted with the silica having hydroxyl group. This kind of side reaction could cause process problems during the polymerization reaction as it could possibly be leached out, when it was activated with aluminoxane. The polymer may show different characteristics from the one obtained from non-supported homogeneous catalyst, thus losing advantages obtainable by homogeneous catalyst system.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for manufacturing a supported metallocene catalyst by reacting metallocene compounds having an alkoxy-silane group with highly reactive siloxane groups, which are produced when the supporting materials are dried at high temperature as in the reaction formula 4, not with OH groups of the supporting materials.

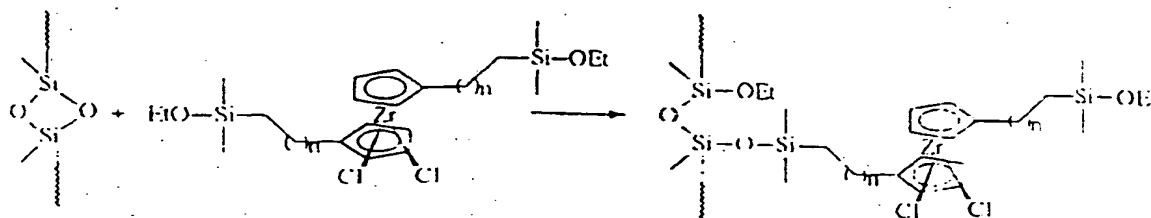
By using this method, supporting materials having much less amount of surface hydroxyl groups should be used in order to eliminate the various side reactions caused by hydroxyl groups.

Also in accordance with the present invention, there is provided a method of manufacturing a supported metallocene catalyst. The method includes the step of reacting a silica with using a metallocene catalyst having an alkoxy-silane group. The silica has siloxane groups with high activity on the

surface thereof by drying a silica at a temperature above 600 °C.

Still further in accordance with the present invention there is provide a method of polymerizing olefinic monomer. The method includes the step of polymerizing olefinic monomers by using a supported metallocene catalyst and a cocatalyst. The supported metallocene catalyst is prepared by reacting a silica with a metallocene catalyst having an alkoxy silane group. The silica has siloxane groups with high activity on the surface thereof by drying a silica at a temperature above 600 °C.

<Reaction formula 4>



10

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying graph, wherein:

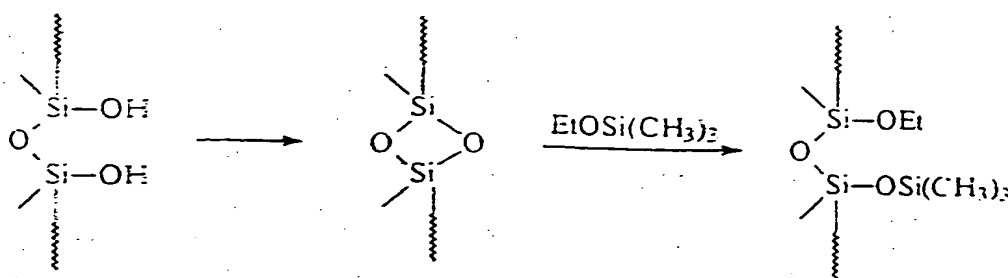
FIG. 1 is a graph showing the relation with hydroxyl group of silica surface and activity of catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a supporting method decreasing various side reactions by using support having less surface OH groups. When silica is dried at a high temperature, surface hydroxyl groups are removed into water generating siloxane groups like the below reaction formula 3. It has been reported that with drying temperatures of 200 ~ 500 °C, easily removable hydroxyl groups are reversibly removed to generate a low reactive siloxane group, but in case of drying temperatures over 600 °C, hydroxyl groups are

forcibly removed into water to generate a siloxane group, which has high ring strain and very high reactivity (I. - S. Chuang and G. E. Maciel, Journal of American Chemical Society, 1996, vol. 118, 401). Highly reactive siloxane groups, produced by drying at over 600 °C, were reported to react with alkoxy silane group as the following reaction formula 3 (J. Blumel, Journal of American Chemical Society, 1995 vol. 117, 2112; L. H. Dubois, Journal of American Chemical Society, 1993, vol. 115, 1190).

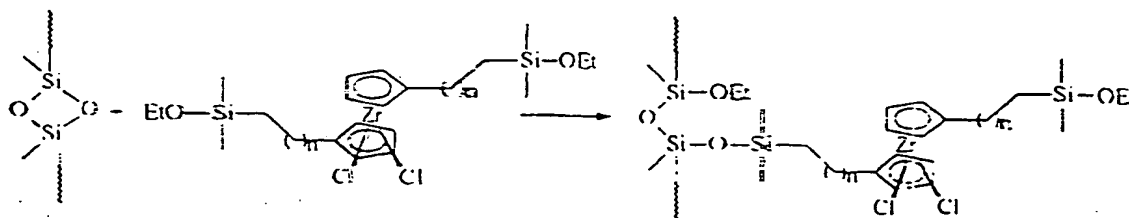
<Reaction formula 3>



10 The present invention is characterized in supporting the metallocene compounds by reacting metallocene catalyst having alkoxy silane group with the highly reactive siloxane group of the supporting materials as shown in reaction formula 4, not with surface OH groups.

By using this method, supporting materials having much less amount of surface hydroxyl groups are used in order to eliminate the various side reactions caused by hydroxyl groups.

<Reaction formula 4>

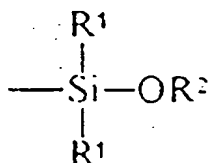


20 The present invention is described in detail as follows. Catalyst having alkoxy silane group, which is usable in the present invention, is generally as

follows:

Compound, where at least more than one of hydrogen radicals among R^3 , R^4 and B in the compounds depicted Formula 2 or 3, which show the activity for the olefin polymerization when activated with cocatalyst, were substituted with radical depicted below Formula 1.

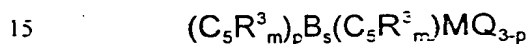
[Formula 1]



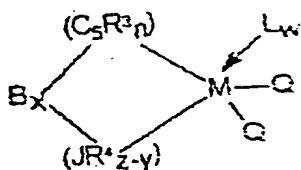
where R^1 is selected from the group consisting of a hydrogen radical, an alkyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms, a halogen radical, and an alkoxy radical of 1 to 20 carbon atoms; and

R^2 is selected from the group consisting of an alkyl radical, an arylalkyl radical, an alkylaryl radical, and an aryl radical, of 1 to 20 carbon atoms.

[Formula 2]



[Formula 3]



where M is a transition metal of Group IVB of the Periodic Table;

$(C_5R^3_m)$ or $(C_5R^3_n)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R^3 which can be the same or different, is a hydrogen radical, an alkyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms, a halogen radical, and an alkoxy radical of 1 to 20 carbon atoms, or a metalloid radical of metal of Group 14 (IvB in the previous IUPAC form)

substituted with hydrocarbyl group, a cyclopentadienyl or substituted cyclopentadienyl ligand in which two adjacent carbon atoms are joined together to form one or more C_4-C_8 rings by a hydrocarbyl radical;

B is a bridge joining two cyclopentadienyl ligands or a cyclopentadienyl ligand and JR^4_{z-y} by a covalent bond, which is selected from the group of consisting of an alkylene radical of 1 to 4 carbon atoms, a dialkylsilicone radical, a dialkylgermanium radical, an alkyl phosphine radical, or an amine radical

R^4 is selected from the group of consisting of a hydrogen radical, an alkyl radical, an alkenyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms;

J is an element of Groups VA or VIA of the Periodic Table;

Q is the same or different halogen radical, an alkyl radical, an alkenyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, or alkylidene radical, of 1 to 20 carbon atoms;

L is a Lewis base and w is greater than 0;

s is 0 or 1, p is 0, 1 or 2, when p is 0, s is 0, when s is 1, m is 4, and when s is 0, m is 5;

z is a valence number of J, and is 3 for element of Group VA, and 2 for Group VIA; and

x is 0 or 1, when x is 0, n is 5, y is 1, when x is 1, n is 4, y is 2.

The Molecular structure of representative metallocene catalysts which can be used in the present invention is described at Table 1. However, it is not limited to this, as here X is ethoxy or methoxy and n is possibly 1 ~ 20.

As has been reported by R. Jackson etc., (R. Jackson, J. Ruddlesten. And D. J. Thompson, R. Whelan, J. Organomet. Chem. 125 (1997). 57; B. L. Booth. G. C. Ofunne. C. Stacey, and P. J. T. Tait, J. Organomet. Chem. 135 (1986), 145; European Patent No. 293815), metallocene catalyst can be synthesized by metallation of the cyclopentadienyl ligands having an alkoxy silane group, but more easily synthesized in hydrosilylation of the metallocene compounds having alkenyl or alkynyl group.

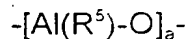
A supporting material having a highly reactive siloxane group on its

surface produced by drying at high temperature is used in the present invention in detail, silica-alumina, silica-magnesia, etc. dried at a high temperature could be used and these generally contain an oxide compound, and a carbonate, a sulfate, and a nitrate consisting of Na_2O , K_2CO_3 , BaSO_4 , $\text{Mg}(\text{NO})_2$, etc. The most major characteristics of the present invention is to use a support having a highly reactive siloxane group on its surface which is dried at high temperatures with flowing air, nitrogen, and inert gas or at reduced pressure, removing water and OH groups on that supporting materials. The preferred drying temperature is over 600 °C. The less amount of OH group on the surface, the better. However, it is practically difficult to remove all OH groups. The amount of OH groups is preferably less than 0.5 mmol/g. The amount of surface OH groups can be controlled by the drying temperature, drying time, drying method, etc. In order to reduce the side reaction by some remaining OH groups, a support may be chemically modified to transform OH to other unreactive group such as OSiMe_3 group.

Supported catalyst is manufactured by reacting the above described catalyst with a support. As a solvent, most of organic solvents including an aliphatic hydrocarbon solvent; like hexane or pentane, an aromatic hydrocarbon solvent; like toluene or benzene; a chlorine atom substituted hydrocarbon solvent, like dichloromethane, an ether base solvent, like diethylether or tetrahydrofuran, acetone, ethylacetate, etc., can be used. However, hexane, heptane, toluene, and dichloromethane are the most desirable. Reaction without solvents is also possible. Although possible reaction temperatures range from -30 °C to 150 °C, The preferable temperature is from room temperature to 100 °C. After filtering reacting solvents, removing through reduced distillation, and Soxhlet filtering with toluene if necessary, the reacted supporting catalyst itself could be used.

This manufactured supported catalyst could be used in the olefin polymerization by activation with compounds represented in Formulae 4, 5, or 6 respectively or by using the mixture thereof.

<Formula 4>



Wherein, each R^5 , which can be the same or different, is selected from a group comprising halogen, hydrocarbyl radicals having from 1 to 20 carbon atoms, or substituted hydrocarbyl radicals having 1 to 20 carbon atoms substituted by a halogen. The subscript a is an integral number over 2, and this compound can exist in a linear, circular, or network structure.

<Formula 5>



Wherein N is aluminum or boron, R^5 is defined the same as in the above described Formula 5, with each three of R^5 groups can be the same or different.

<Formula 6>



Wherein L is a neutral or positive ionic Lewis acid, H is a hydrogen atom, N is an element of Group 13 (IIIb in the previous IUPAC form), e.g., aluminum and boron, each E , which can be the same or different, is an aryl radical having from 6 to 20 carbon atoms, where more than one hydrogen radical were substituted with halogen radical, alkoxy radical, or phenoxy radical.

Examples of compound described in the above Formula 4 include methylaluminoxane, ethylaluminoxane, isobutylaluminoxane, butylaluminoxane, etc. Examples of alkyl metal compounds described in the above Formula 5 include trimethylaluminum, triethylaluminum, triisobutylaluminum, tripropylaluminum, tributylaluminum, dimethylchloroaluminum, triisopropylaluminum, tri-*s*-butylaluminum, tricyclopentylaluminum, tripentylaluminum, triisopentylaluminum, trihexylaluminum, ethyldimethylaluminum, methyldiethylaluminum, triphenylaluminum, tri-*p*-tolylaluminum, dimethylaluminummethoxide, dimethylaluminummethoxide, trimethylboron, triethylboron, triisobutylboron, tripropylboron, tributylboron, etc.

Examples of compound in Formula 6 include triethylammoniumtetraphenylboron, tributylammoniumphenylboron, trimethylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammoniumtetra(p-tolyl)boron, trimethylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, trimethylammoniumtetra(p-trifluoromethylphenyl)boron, tributylammoniumtetraphentafluorophenylboron, N,N-diethylammoniumtetraphenylboron, N,N-diethylanilidiumtetraphenylboron, N,N-diethylaniliumtetraphentafluorophenylboron, diethylammoniumtetraphentafluorophenylboron,

10 triphenylphosphoniumtetraphenylboron, trimethylphosphoniumtetraphenylboron, triethylammoniumtetraphenylaluminum, tributylammoniumtetraphenylaluminum, trimethylammoniumtetraphenylaluminum, tripropylammoniumtetraphenylaluminum, trimethylammoniumtetra(p-tolyl)aluminum, triethylammoniumtetra(o,p-dimethylphenyl)aluminum, tributylammoniumtetra(p-trifluoromethylphenyl)aluminum,

15 trimethylammoniumtetra(p-trifluoromethylphenyl)aluminum, tributylammoniumtetrapentafluorophenylaluminum, N,N-diethylanniliumtetraphenylaluminum, N,N-diethylanniliumtetraphenylaluminum, N,N-diethylanniliumtetrapentafluorophenylaluminum,

20 diethylammoniumtetrapentafluorophenylaluminum, triphenylphosphoniumtetraphenylaluminum, trimethylphosphoniumtetraphenylaluminum, triethylammoniumtetraphenylaluminum, tributylammoniumtetraphenyltetraphenylaluminum,

25 trimethylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammoniumtetra(p-tolyl)boron, tripropylammoniumtetra(p-tolyl)boron, triethylammoniumtetra(o,p-dimethylphenyl)boron, trimethylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, trimethylammoniumtetra(p-trifluoromethylphenyl)boron,

30 tributylammoniumtetrapentafluorophenylboron, N,N-diethylanniliumtetraphenylboron, N,N-diethylanniliumtetraphenylboron, N,N-

diethylanniliumtetrapentafluorophenylboron,
diethylammoniumtetrapentafluorophenylboron,
triphenylphosphoniumtetraphenylboron, triphenylcarboniumtetra(p-
trifluoromethylphenyl)boron, triphenylcarboniumtetrapentafluorophenylboron,
5 etc.

Solvents used when manufacturing olefin based polymer by using the
above described supported catalyst and cocatalyst include aliphatic hydrocarbon
solvents, e.g., pentane, hexane, heptane, nonane, decane, and their isomers and
aromatic hydrocarbonate solvents, like toluene or benzene, chlorine atom
10 substituted hydrocarbon solvents, like dichloromethane or chlorobenzene, and
mixtures of two or more of these solvents.

Examples of olefin based monomer, which is capable of polymerization
by using the above described support catalyst and cocatalyst, include ethylene,
 α -olefin, cyclic olefin, etc., diene monomers having more than two double bonds
15 or triene monomers, etc., are also capable of polymerization.

Examples of the above described monomers include ethylene,
propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-
decene, 1-undecene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-icosene,
nonylene, nonadiene, ethylenononylene, vinylnonylene, dicyclopentadiene,
20 1,4-butadiene, 1,5-pentadiene, 1,6-hexadiene, styrene, α -methylstyrene,
divinylbenzene, 3-chloromethylstyrene, etc. Copolymerization could be done
by mixing more than one of these monomers.

Polymerization is performed at temperature ranging from 25 °C to
500 °C and the pressures ranging from 40 psi to 800 psi. It is preferable to
25 add catalyst in an amount that is 1 to 30,000 times the metallocene mole content.
In the present invention, contact order and input order of catalyst, cocatalyst,
solvent, and monomer are not particularly restricted. That is, polymerization is
done by putting the above described support catalyst and cocatalyst into
suspension solvents simultaneously, or main polymerization could be done after
30 either the activation reaction or prepolymerization. Prepolymerized catalyst can
be obtained by filtering or decanting after stirring of supported catalyst activated

with cocatalyst in the presence of olefin under the appropriate temperature and pressure. Activated catalysts can be obtained as the same method of prepolymerization reaction without olefin.

Although the present invention is illustrated by the following practical exercises in detail, the range of the present invention is not limited by these practical exercises.

Example 1

Organic reagents and solvents, which are needed in catalyst manufacturing and polymerization, were bought from Aldrich and Merck, refined by standard methods. Ethylene was polymerized after passing high purified products bought from Applied Gas Technology through moisture and oxygen filtering equipment. Test reproductability was increased by blocking contact between air and moisture at all stages of catalyst synthesizing, injecting and polymerizing. Molecular weight of the polymerized polymer was measured by high temperature Gel Permeation Chromatography. It was measured after making universal correction curves of polystyrene standard samples and dissolving polymerized polymer by using Waters' model 150 V attaching a concentration detector capable of measuring refraction ratio and viscosity simultaneously. After dissolving into CDCl_3 solvents a spectrum was obtained by using a 270 MHz Joel Nuclear Magnetic Resonator (NMR) or a 300 MHz Bruker NMR in order to identify the structure of catalysts. The supporting amount of support catalyst was found by measuring the Zr amount with the Inductively Coupled Plasma (ICP) spectroscopic method. The amount of surface silica hydroxyl group was obtained by titrating with MeMgI , following the method J.J. Fripiat and J. Uytterhoeven published in Journal of Physical Chemistry, 66, 800 (1962).

a) Synthesizing of catalysts having an alkoxysilane group:

1) Synthesizing of $[\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{C}_5\text{H}_4]_2\text{ZrCl}_2$

9-hexene-1-ol 10.36 g, paratoluenesulfonylchloride 24.11 g and diethylether 200 ml was put into one opening flask and mixed well. Well grounded high temperature powder of potassium hydroxide 353.5 g was slowly

added at temperature for about 10 minutes after decreasing the temperature of the flask to -10°C by dipping it into the low temperature vat. It was then agitated at -15°C to -5°C for about 30 minutes. After that, this solution was poured into 200 ml of cold iced water. After collecting ester layers by fractional funnelling and removed moisture by inserting anhydrous magnesium sulfate, magnesium sulfate was removed by filtering to obtain a colorless viscous compound solution a 200 ml shrank flask. Ether was removed with reduced a pressure rotational distiller. Anhydrous THF (Tetrahydrofuran) 120 ml was then poured into a Schlenk flask containing this compound. After this, the flask was dipped into an iced low temperature vat, and NaCp (2 M, tetrahydrofuran) 62 ml was injected into the flask. It was then agitated at the room temperature for about 3 to 5 hours after removing the iced low temperature vat. Organic layers were mixed and collected after pouring this solution into a 1 liter fractional funnel, filled with 200 ml of water and 200 ml of hexane. Magnesium sulfate was removed by removing moisture and filtering after putting anhydrous magnesium sulfate into the organic layers. All solvents were removed with a reduced pressure distiller. A somewhat yellow liquid compound was obtained and 9.643 g of hexenylcyclopentadien compound was obtained by vacuum distillation (yield: 65 %).

The above manufactured 9.643 g of decenylcyclopentadien and 100 ml of THF (tetrahydrofuran) were put into a 250 ml Schlenk flask. After decreasing temperature of this to -78°C with a aceton-dryice low temperature vat, 26 ml of n-butyllitium (2.5 M, hexane solution) was slowly supported during agitation. The temperature was increased to room temperature and it was agitated overnight at a room temperature. After weighing in the dry box, 12.26 g $\text{ZrCl}_4(\text{THF})_2$ was made from ZrCl_4 compound according to the method described in Inorganic Synthesis 1982, vol. 21, 135, by putting it into a 500 ml Schlenk flask with, 200 ml of anhydrous toluene. Then THF (tetrahydrofuran) solution, which has been agitated all night, and toluene solution were mixed, where $\text{ZrCl}_4(\text{THF})_2$ was contained without air contact at a room temperature.

This mixture was agitated at 50 to 60 °C for 3 days. Solvents were removed by vacuum after lowering the temperature to 40 °C. 20 ml of hexane were heated somewhat to melting formed solid material and then filtered while in the heated state without air contact. Hexane again was removed from the filtered solution by vacuum pump and the desired white solid compound was obtained. The yield was 65 %.

^1H Nuclear Magnetic Resonator analysis (300 MHz, CDCl_3) : 6.27 (2 H, t, $J=2.6$ Hz), 6.18 (2 H, t, $J=2.6$ Hz), 5.77 (1 H, ddt, $J=7.5$ Hz), 2.1-2.0 (2 H, t, $J=7.5$ Hz), 2.1-2. (2 H, m), 1.6-1.3 (4 H, m);

^{13}C Nuclear Magnetic Resonator analysis (CDCl_3) : 138.6, 134.9, 116.7, 114.5, 112.2, 33.4, 30.1, 30.0, 28.5.

2) Synthesizing of $[\text{Cl}(\text{Me})_2\text{Si}-(\text{CH}_2)_6\text{C}_5\text{H}_4]_2\text{ZrCl}_2$

After weighing in the dry box the above 1.28 g of synthesized $[\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{C}_5\text{H}_4]_2\text{ZrCl}_2$ was put it into 100 ml Shrank flask. After taking it out of the dry box, 5 ml of toluene 5 ml and 1.2 ml of chlorodimetalsilane are added while agitating. It was then gitated at a room temperature for one day after putting 20 ml of H_2PtCl_6 isopropanol solution (0.1 M). All solvents were removed with a vacuum pump, and it was then heated somewhat with 100 ml of hexane to melt solids that have formed. It was filtered in the hot state, the filtered solution put in the refrigerator, and left alone for one day, obtaining a white crystal (yield: 90 %).

^1H Nuclear Magnetic Resonator analysis (500 MHz, CDCl_3) : 6.27 (2 H, t, $J=2.4$ Hz), 6.18 (2 H, t, $J=2.4$ Hz), 2.60 (2 H, t, $J=7.5$ Hz) 1.7-1.45 (2 H, m), 1.45-1.1 (4 H, m), 0.85-0.75 (2 H, m), 0.37 (6 H, s);

^{13}C Nuclear Magnetic Resonator Analysis (CDCl_3) : 134.9, 116.6, 112.2, 32.5, 30.3, 30.0, 22.8, 18.8, 1.6.

3) Synthesizing of $[(\text{EtO})(\text{Me})_2\text{Si}-(\text{CH}_2)_5\text{C}_5\text{H}_4]_2\text{ZrCl}_2$

After putting 4.7 ml of trimethylorthoformate into the above manufactured 1.63 g of $[\text{Cl}(\text{Me})_2\text{Si}-(\text{CH}_2)_6\text{C}_5\text{H}_4]_2\text{ZrCl}_2$ compound, the mixture was agitated well and about 1 mg of anhydrous AlCl_3 was added and the reaction

progress with gas appearing. About two hours later, gassing stopped. After the removal of all volatile materials, 30 ml of hexane was added and dissolved. After filtering and removing all solvents with a vacuum pump, an oily solid compound (yield 1.60 g, 95 %) was obtained.

5 ^1H Nuclear Magnetic Resonator Analysis (300 MHz, CDCl_3) : 6.27 (2H, t, $J=2.7$ Hz), (2H, t, $J=2.7$ Hz), 3.62 (2 H, q, $J=7.2$ Hz), 2.60 (2 H, t, $J=7.5$ Hz) 1.7-1.2 (16 H, m), 1.16 (3 H, t, $J=7.2$ Hz), 0.65-0.45 (2 H, m) 0.06 (6 H, s);

^{13}C Nuclear Magnetic Resonator Analysis (CDCl_3) : 135.1, 116.6, 112.3, 58.1, 33.1, 30.2, 30.2, 29.0, 23.1, 18.5, 16.3, 0.37.

10 b) Drying of silica

After weighing, 2.0 g of Grace Davison 948 silica was put into a crystal container, and placed into a furnace manufactured by Lindberg, where the temperature was increased at the rate of 7 $^\circ\text{C}/\text{min}$ reaching 800 $^\circ\text{C}$ and then cooled from this temperature for 21 hours. Using the same method, silica was
15 dried at 200 $^\circ\text{C}$, 400 $^\circ\text{C}$ and 600 $^\circ\text{C}$.

c) Drying of support catalyst

The silica dried at b) above was moved from the dry box to a Schlenk flask and sealed, in order to be taken out. A solution (concentration : 37 $\mu\text{g}/\text{ml}$) in which catalyst, $[(\text{EtO})(\text{Me})_2\text{Si}-(\text{CH}_2)_6\text{C}\equiv\text{C}_4\text{H}_9]_2\text{ZrCl}_2$, was dissolved in hexane was
20 and made 3.6 ml of this solution (2.0 mmol) and 30 ml of hexane were mixed. This slurry was refluxed for 18 hours. Hexane was removed by distilling at a vacuum, this support catalyst was extracted for two days by using a Soxhlet's extractor and using toluene as a solvent. All catalysts which were not supported by the characteristic bond were removed. The amount of support
25 catalyst according to the drying temperature is represented in Table 2.

d) Polymerization

After weighing 100 mg of support catalyst manufactured at c) in the dry box, it was put into a glass reactor, sealed in the reactor and taken out of the dry box. 200 ml of refined hexane were put into this reactor and placed in 2.0 ml of
30 aluminoxane MMAO-3 (6. % Al) melted in haptan manufactured by Akzo. After

agitating at 80 °C for 5 minutes, ethylene was poured in under the pressure of 40 psig. This was polymerized for one hour at this temperature and pressure. The reaction was finished by putting 5 ml of ethanol into the reactor. Polymer was obtained after filtering and drying in an 80 °C oven. The polymer amount, activity, polymer molecular weight, and molecular weight distribution according to the drying temperature of silica are represented in Table 1.

Table 1 shows the relation between drying temperature and amount of hydroxyl group, support amount of catalyst obtained at this time, activity, molecular weight of polymer obtained by this supported catalyst, and molecular weight distribution.

[Table 1]

Drying temperature (°C)	OH amount mmol/g	Supported amount Zr %	Polymer amount g	Activity KgPE/Zr h	Molecular weight Mw	Molecular weight distribution Mw/Mn
200	11.8	1.1	6.7	0.56	324500	3.37
400	0.85	1.1	8.7	0.73	328000	0.63
600	0.54	0.98	13.6	1.2	192000	2.79
800	0.35	0.85	13.7	1.5	189000	2.64

It is shown that as expected the higher the drying temperature is, the less the amount of hydroxyl groups. Although the deposit amount is also somewhat decreased as the amount of surface hydroxyl groups decreases, there is not much affect because catalyst can be deposited by the reaction with a hydroxyl group, and deposit is also possible by the reaction with high reactive siloxane group. As it is noted in Figure 1, the fact that the less the amount of hydroxyl group becomes, the more the amount of monomer obtained and the more metal activities increase means the deposited catalyst reacted by reacting with hydroxyl groups as expected with large non-active areas due to side reactions, and on the contrary, deposited catalyst by siloxane groups shows most of activities due to less side reactions. The fact that the less hydroxyl

group the more narrow molecular weight distribution, an inherent characteristic of metallocene catalyst, means deposited catalyst by siloxane groups is attached as a desired form, and deposited catalyst by hydroxyl groups change into various forms of catalysts by side reactions. That is, Table 1 and Figure 1 show
5 there is more advantages in activity and molecular weight distribution when depositing metallocene catalyst having an alkoxysilane group, an important characteristic of the present invention, having small hydroxyl groups and high reactive siloxane groups than when using the existing hydroxyl groups. Particularly, it is noted that when the amount of hydroxyl group is lower than 0.5
10 mmol/g, which is limited in European Patent No. 293815, metal activities are maximized and Mw/Mn shows minimum values.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the
15 spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1 A method of manufacturing a supported metallocene catalyst comprising the step of:

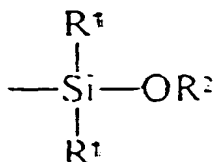
reacting a silica with using a metallocene catalyst having an alkoxysilane group, the silica having siloxane groups with high activity on the surface thereof
5 by drying a silica at a temperature above 600°C.

2. A method of an polymerizing olefinic monomer comprising the step of:

polymerizing olefinic monomers by using a supported metallocene catalyst and a cocatalyst, the supported metallocene catalyst being prepared by
10 reacting a silica with a metallocene catalyst having an alkoxysilane group and the silica having siloxane groups with high activity on the surface thereof by drying a silica at a temperature above 600°C.

3. The method according to claim 2 wherein the supported catalyst
15 is prepared by contacting a silica with a metallocene compound, the silica having siloxane groups with high activity on the surface thereof by drying the silica at a temperature above 600 °C and the compound being prepared by substituting a hydrogen radical in R³, R⁴ and B of a compound of Formula 2 or a compound of Formula 3 with at least one radical of Formula 1 and the cocatalyst is the
20 compound depicted by Formula 4 or Formula 5 or a mixture of thereof;

[Formula 1]

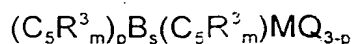


where R¹ is selected from the group consisting of a hydrogen radical, an alkyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20
25 carbon atoms, a halogen radical, and an alkoxy radical of 1 to 20 carbon atoms; and

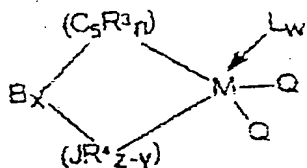
R² is selected from the group consisting of an alkyl radical, an arylalkyl

radical, an alkylaryl radical, and an aryl radical, of 1 to 20 carbon atoms.

[Formula 2]



[Formula 3]



5

where M is a transition metal of Group IVB of the Periodic Table;

$(C_5R^3_m)$ or $(C_5R^3_n)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R^3 which can be the same or different, is a hydrogen radical, an alkyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms, a halogen radical, and an alkoxy radical of 1 to 20 carbon atoms, or a metalloid radical of metal of Group 14 (IvB in the previous IUPAC form) substituted with hydrocarbyl group, a cyclopentadienyl or substituted cyclopentadienyl ligand in which two adjacent carbon atoms are joined together to form one or more C_4 - C_8 rings by a hydrocarbyl radical;

15 B is a bridge joining two cyclopentadienyl ligands or a cyclopentadienyl ligand and JR^4_{z-y} by a covalent bond, which is selected from the group of consisting of an alkylene radical of 1 to 4 carbon atoms, a dialkylsilicone radical, a dialkylgermanium radical, an alkyl phosphine radical, or an amine radical

R^4 is selected from the group of consisting of a hydrogen radical, an alkyl radical, an alkenyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms;

J is an element of Groups VA or VIA of the Periodic Table;

Q is the same or different halogen radical, an alkyl radical, an alkenyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, or alkylidene radical, of 1 to 20 carbon atoms;

25

L is a Lewis base and w is greater than 0;

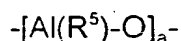
s is 0 or 1, p is 0, 1 or 2, when p is 0, s is 0, when s is 1, m is 4, and

when s is 0, m is 5;

z is a valence number of J, and is 3 for element of Group VA, and 2 for Group VIA; and

x is 0 or 1, when x is 0, n is 5, y is 1, when x is 1, n is 4, y is 2.

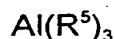
5 <Formula 4>



wherein each R^5 , which can be the same or different, is selected from a group comprising a halogen radical, hydrocarbyl radical having from 1 to 20 carbon atoms or halogen substituted hydrocarbyl radical having from 1 to 20
10 carbon atoms;

a is an integral number more than 2, this compound can be existed as linear, circular or network form.

<Formula 5>



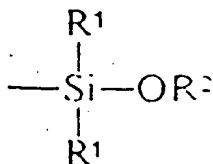
15 Wherein R^5 is defined the same as in the above described Formula 4, each three of R^5 can be either the same or different.

4. The method according to claim 3 wherein R^3 and B of the compound of formula 2 is substituted with a radical of Formula 1.

5. The method according to claim 4 wherein the compound of
20 Formula 2 has s of 0 and p of 1.

6. The method according to claim 2 wherein the supported catalyst is prepared by contacting a silica with a metallocene compound, the silica having siloxane groups with high activity on the surface thereof by drying a silica at a temperature above 600 °C and the compound being prepared by substituting a
25 hydrogen radical in R^3 , R^4 and B of a compound of Formula 2 or a compound of Formula 3 with at least one radical of Formula 1 and the cocatalyst is the compound depicted by Formula 6:

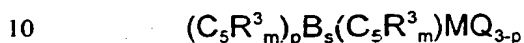
[Formula 1]



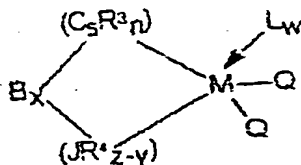
where R¹ is selected from the group consisting of a hydrogen radical, an alkyl radical, an arylalkyl radical, an alkylaryl radical, an aryl radical, of 1 to 20 carbon atoms, a halogen radical, and an alkoxy radical of 1 to 20 carbon atoms; and

R² is selected from the group consisting of an alkyl radical, an arylalkyl radical, an alkylaryl radical, and an aryl radical, of 1 to 20 carbon atoms.

[Formula 2]



[Formula 3]



wherein Formula 1, 2 and 3 are defined the same as in claim 3;

<Formula 6>



wherein L is a neutral or a positive ionic Lewis base, H is a hydrogen atom;

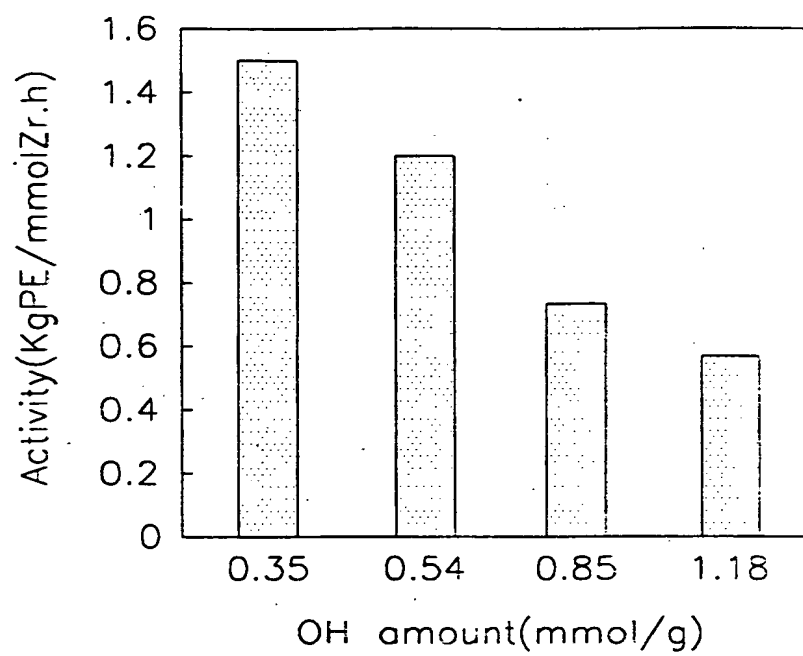
N is an element of Group 13 (IIIb in the previous IUPAC form);

Each E, which can be the same or different, is an aryl radical having from 6 to 20 carbon atoms, where more than one hydrogen radical were substituted with halogen radical, alkoxy radical, or phenoxy radical.

7. A method according to claim 6 wherein the R³ and B of the compound of Formula 2 is substituted with a radical of Formula 1.

8. A method according to claim 6 wherein the compound of Formula 2 has s of 0 and p of 1.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KP 99/00169

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 02 F 4/602; C 07 F 17/00; C 08 F 10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols).

IPC⁶: B 01 J; C 07 F; C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used):

WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 293 815 A1 (HOECHST AKTIENGESSELLSCHAFT), 07 December 1988 (07.12.88), page 5, line 16-18; examples 2,3.	1-8
A	EP 0 821 009 A1 (DAELIM INDUSTRIAL CO.,LTD.), 28 January 1998 (28.01.98), examples 2,3; claims 1,2.	1-8
A	EP 0 799 838 A1 (MIKROKEMIA OY), 08 October 1997 (08.10.97), page 6, lines 31-37; page 8, lines 31-35, 46-55; examples 2-4; claims 1-22.	1-8
A	EP 0 799 641 A2 (MIKROKEMIA OY), 08 October 1997 (08.10.97), page 7, lines 26-32; page 11, lines 12-15; examples 1, 10,11; claims 1,2,5,19.	1-8
A	EP 0 628 566 A1 (PHILLIPS PETROLEUM COMPANY), 14 December 1994 (14.09.94), page 5, lines 52-54; claims 1-22.	1-8

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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- ☐ document referring to an oral disclosure, use, exhibition or other means
- ☐ document published prior to the international filing date but later than the priority date claimed

..T.. later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

..X.. document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

..Y.. document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

..&.. document member of the same patent family

Date of the actual completion of the international search

19 May 1999 (19.05.99)

Date of mailing of the international search report

23 July 1999 (23.07.99)

Name and mailing address of the ISA/AT

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Pusterer

Telephone No. 1 53424/511

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 99/00169

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 757 053 A2 (HOECHST AKTIENGESELLSCHAFT), 05 February 1997 (05.02.97), page 7, lines 31-33; claims 1-5. -----	1-8

International application no.

[illegible]

International application No.

PCT/KR 99/00189

[illegible]

ECT/KR 22/00122

Form PCT/ISA/210 (parent family annex) (July 1998)